PCT
WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : C08L 67/02

A1

(11) International Publication Number: WO 94/09069

(43) International Publication Date: 28 April 1994 (28.04.94)

(21) International Application Number: PCT/EP93/02834

(22) International Filing Date: 14 October 1993 (14.10.93)

(30) Priority data:
MI92A002373 15 October 1992 (15.10.92) IT

(71) Applicant (*for all designated States except US*): M. & G. RICERCHE S.P.A. [IT/IT]; Località Triverno - Zona Industriale, I-86077 Pozzilli (IT).

(72) Inventor; and
(75) Inventor/Applicant (*for US only*) : AL GHATTA, Hussain, Ali, Kashif [IQ/IT]; Via delle Piagge, 12, I-03014 Fiuggi (IT).

(74) Agents: GERBINO, Angelo et al.; Jacobacci-Casetta & Perani S.p.A., Via Alfieri, 17, I-10121 Torino (IT).

(81) Designated States: CA, JP, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: POLYMERIC ALLOYS FROM POLYESTER RESINS AND PROCESS FOR THEIR PREPARATION

(57) Abstract

Process for the preparation of polymeric alloys from polyester resins and polymers containing groups capable of giving addition reaction with functional compounds containing at least two reactive groups comprising the melt state mixture stage of polyester resin, reactive polymer and functional compound of mixture pelletizing and following polyaddition reaction in the solid state at temperatures between 150 ° and 220 °C to obtain an increase of the polymer intrinsic viscosity of 0.1 dl/g in comparison with the starting polyester resin.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	MR	Mauritania
AU	Australia	GA	Gabon	MW	Malawi
BB	Barbados	GB	United Kingdom	NE	Niger
BE	Belgium	GN	Guinea	NL	Netherlands
BF	Burkina Faso	GR	Greece	NO	Norway
BG	Bulgaria	HU	Hungary	NZ	New Zealand
BJ	Benin	IE	Ireland	PL	Poland
BR	Brazil	IT	Italy	PT	Portugal
BY	Belarus	JP	Japan	RO	Romania
CA	Canada	KP	Democratic People's Republic of Korea	RU	Russian Federation
CF	Central African Republic	KR	Republic of Korea	SD	Sudan
CG	Congo	KZ	Kazakhstan	SE	Sweden
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovak Republic
CM	Cameroon	LU	Luxembourg	SN	Senegal
CN	China	LV	Latvia	TD	Chad
CS	Czechoslovakia	MC	Monaco	TG	Togo
CZ	Czech Republic	MG	Madagascar	UA	Ukraine
DE	Germany	ML	Mali	US	United States of America
DK	Denmark	MN	Mongolia	UZ	Uzbekistan
ES	Spain			VN	Viet Nam
FI	Finland				

Polymeric alloys from polyester resins and process for their preparation

The present invention relates to an improved process for the preparation of polymeric alloys from polyester resins and polymers containing reactive end groups.

The polymeric alloys from polyester resins and from resins such as polycarbonate, polyamides were so far obtained by blending in the molten state optionally operating in the presence of functional compounds able to react with the resin end groups.

The properties of these alloys are not satisfactory due to side reactions such as transesterification, transamidation and degradation, which occur in the molten state. Due to the degradation reactions, it was not possible moreover to prepare resins with molecular weight high enough to enable good mechanical properties of the polymeric alloys.

A method has now been found which allows to prepare polymeric alloys with unexpectly high mechanical properties by reacting resins mixtures at the solid state in the presence of a polyfunctional compound containing at least two groups capable of reacting with addition reactions with the resins end groups.

The polyester resin, the resin containing reactive groups and the functional compound are blended in the molten state; the mixture is then pelletized and the chips are then subjected to the solid state polyaddition reaction.

The polyaddition reaction in the solid state is generally preceded by a crystallization step carried out after the melt state mixture stage and after the following pelleti-

zing. The crystallization step is carried out to prevent agglomeration phenomena of chips and/or of sticking on the reactor wall during the reaction in the solid state.

The crystallization step is carried out at temperatures higher than the TG of the polyester and comprised in general between 130° and 180°C.

The process of alloys preparation is preferably carried out in continuous way using continuous crystallizers and polyaddition reactors where the chips are fed counter currently to a stream of a heated gas, e.g. air, nitrogen and other inert gas, such as carbon dioxide. The polyaddition reaction in the solid state is carried out at temperatures higher than 150°C and lower than the melting point of the polyester resins. The temperatures are in general comprised between 180° and 210°C. The residence time depends on the increase of the required intrinsic viscosity and of the mechanical properties. The viscosity increase is at least 0.1 dl/g in comparison with the starting polyester resin. The treatment is carried out in an inert gas stream in a fluid bed or fluidized reactor.

The polyfunctional compound is preferably selected from the group consisting of pyromellitic acid dianhydride, 3,3' 4,4' biphenyltetracarboxylic acid, bis (3,4-dicarboxyphenyl) ether, bis (3,4 dicarboxyphenyl) thiother, 3,4 dicarboxylic acid, bisphenol A, 2,2 - bis (3,4 dicarboxyphenyl) hexafluoropropane, 2,3,6,7 naphtalenetetracarboxylic acid, bis (3,4 dicarboxyphenyl) sulfone, 1,2,5,6 - naphtalenetetracarboxylic

acid, 3,2' 3,3' - biphenyltetracarboxylic acid, bis (3,4 dicarboxyphenyl) sulfoxide, 3,4,9,10 - perylene tetracarboxylic acid and mixtures thereof.

The aromatic dianydrides most preferred are the pyromellitic dianydride and 3,3' 4,4' benzophenonetetracarboxylic acid dianydride and mixtures thereof.

Besides the dianydrides of the above mentioned tetracarboxylic aromatic acids can be also used the dianydrides of aliphatic, cycloaliphatic and tetrahydrofurantetracarboxylic acids.

Representative compounds are 1,2,3,4 cyclobutanetetracarboxylic acid and tetrahydrofuran 2,3,4,5 - tetracarboxylic acid.

The blending of the polyester resin with the resins containing reactive end groups and with polyfunctional compound is preferably carried out in corotating or counter rotating, intermeshing or not intermeshing twin screw extruders with or without degassing equipment, at a temperature between 200° and 350°C depending on the melting point of the mixture of the polymers.

A counter rotating and not intermeshing screws extruder is preferred.

The use of such a type of extruder allows to perform a good distribution of the polyfunctional compound in the melt and to avoid problems of local high concentrations of the additive due to its high reactivity.

This type of extruder allows very short residence times.

The extruder is preferably connected with a high vacuum oil seal pump to maintain a vacuum higher than 2 tor to carry out the dosing of the reactive mixture and to obtain a resin with a low content of acethaldehyde.
The preferred concentration of additive with respect to the polyester resin is 0.05-1% by weight.
The residence time in the extruder can be comprised between 10 and 120 sec. preferably 15-30 sec.
To avoid random local concentrations of additive in the melt it is advisable to dilute the additive with crystallized PET powder (1 part of additive to 3 parts of PET powder).
This procedure ensures a homogeneous distribution of additive leading to a better reproducibility of the end product intrinsic viscosity and inhibiting gel formation.
The additive may also be diluted using crystallized PET chips (1 part additive to 10 parts of PET chips).
The blending could be performed in a fanned blender using 0,1% by weight of adhesive agent.
The polyester resins usable in the invention process are the product of polycondensation of glycols with 2-10 carbon atoms, such as ethylene glycol, 1,4-butileneglycol, 1,4 cyclohexylenglycol, with terephthalic acid or derivatives thereof such as dimethylterephthalate, as well as the polycondensation products containing besides units deriving from terephthalic acid, also units deriving from other bicarboxylic acids such as naphthalendicarboxylic acids, isophtalic

acid, orthophtalic acid and 5-tert-butyl-1,3-benzene-dicarboxylic acid in a quantity of about 0.5-25% mole of all acid units.

Among the polyester resins the elastomeric polyester resins are also included and in general are included block polyester copolymers containing blocks deriving from the polycondensation of a glycol with an aromatic bicarboxylic acid.

The starting polyester resin has an intrinsic viscosity lower than 0.8 dl/g and generally between 0.6 and 0.75 dl/g.

The preferred resins are polyethylenterephthalate and copolyethylenterephthalates containing up to 20% of unit deriving from isophtalic acid. The reactive resins different from the polyester resins have end groups preferably selected among OH, NH_2, SH.

The polyamides are the preferred resins. These resins are characterized by the repeating unit - NH CO -; the ponderal molecular weights are generally included between 10,000 and 50,000. Examples of these resins are Nylon 4, Nylon 6,6, Nylon 6, Nylon 8, Nylon 11, Nylon 12.

Other examples of usable resins are polycarbonate, polyphenylenoxide and polysulphide resins. The reactive resins are used in a quantity of about 1-50% preferably 5-20% by weight: on the weight of the mixture.

The alloys obtained using polyamides are characterized by a very high elastic module without sacrificing the tensile strength and elongation at break.Films obtained from alloys prepared starting from polyamides, present values of the

elastic modulus varing between 4.2 and 5 GPa following the stretch ratio in the range between 3-5, while the reference polyester shows values in the range between 3.3 and 2.2 GPa and the alloys obtained without using the polyfunctional compound (piromellitic dianydride) have values of the modulus in the range between 2.4-2.9 GPa.

The following examples are given to illustrate but not to limit the invention.

EXAMPLE 1

10 Kg/h of a mixture at 95% by weight of crystalline PET (IV=0.601 dl/g) and at 5% by weight of 6,6 Nylon (the mixture is dried vacuum at 140°C for 10h) were fed together at 0.05% by weight of pyromellitic dianhydride (PMDA) to a counter rotating and not intermishing twin screw extruder. The mixture was extruded and also pelletized. The chip intrinsic viscosity was 0.694 dl/g; the COOH groups content =52.2 eq/ton. The extrusion conditions were as follows:

Ratio length/diameter (L/D)	= 36
Screw speed	= 150 rpm
Cylinder temperature	= 260°C
Chips feed speed	= 10 Kg/h
PMDA feed speed	= 0.05 Kg/h
mould type	= circular with 3 mm dia.

The so obtained chips were subjected to upgrading at 186°C for 6 hours in nitrogen stream. The intrinsic viscosity after the treatment was of 0,927 dl/g and the COOH groups as 49 eq/ton.

The obtained polymer was then extruded continuously (before drying) in a monoscrew extruder for film. The film was collected on chilled rollers and then on rollers heated at 85°C and then on collecting cylinder. The stretch ratio used was of 3:1 in a test, of 4:1 in a second test and of 5:1 in a third one.

The films mechanical properties are shown in table 1.

Comparative example 1

A mixture at 95% by weight of crystalline PET (IV=0,601 dl/g) and at 5% of 6,6 Nylon (dried vacuum at 140°C for 10h) was extruded and pelletized in the conditions as in example 1.

The chips were then subjected to upgrading under the same conditions as in example 1.

The obtained polymer intrinsic viscosity was of 0,786 dl/g and the groups concentration COOH of 21.4 eq/ton.

The chips were also extruded in the extruder for films of example 1 in the same conditions there indicated. The obtained film was collected with stretch ratio of 3:1, 4:1 and 5:1 in the different tests.

The film properties are shown in table 1

Comparative example 2

PET with IV=0.83 dl/g was filmed under the conditions of example 1 using the same stretch ratios.

The film properties are shown in table 1.

Table 1

Stretch ratio	Module GP a	Tensile strength MP a	Max.strain %
Ex.1			
3	4.2	94	14
4	4.9	163	42
5	5.0	183	22
Ex.1 comparison			
3	2.4	71	91
4	1.9	113	61
5	2.9	189	24
Ex.2 comparison			
3	3.3	103	155
4	3.8	142	69
5	2.2	230	23

The tensile strength was determined according to ASTMD-882 using a INSTRON tensile tester (Mod. 4505) on samples at 25°C and with 50% of relative humidity.

The elastic modulus was determined from the slope at the stress-strain curve.

The intrinsic viscosity was determined in a solution of 0,5 g of polymer in 100 ml, of a solution at 60/40 by weight of phenol and tetraclorethane, operating at 25°C according to ASTM D-4603-86.

CLAIMS

1. Polymeric alloys from polyester resins and reactive polymers containing end groups capable of addition reactions with compounds containing at least two reactive groups obtained by reaction in the solid state of mixtures of the above resins, polymers and functional compounds.
2. Process for the production of polymeric alloys starting from polyester resins and reactive polymers containing end groups capable of addition reactions with functional compounds containing at least two reactive groups according to claim 1, comprising following operations:
   a) blending in the molten state the polyester resin, the reactive polymer and the functional compound
   b) pelletizing the molten mixture
   c) polyaddition treatment in the solid state at temperatures between 150°-220°C for a time sufficient to obtain an increase of at least 0.1 dl/g of the intrinsic viscosity of the polymeric alloy referred to the intrinsic viscosity value of the starting polyester resin.
3. Process according to claim 2, where the reactive polymer contains end groups selected among OH, NH_2 and SH.
4. Process according to claim 2 where the reactive polymer is a polyamide.

5. Process according to claim 4, where the polyamide is chosen among Nylon 4, Nylon 6, Nylon 6,6, Nylon 8, Nylon 11 and Nylon 12.
6. Process according to claims from 1 to 5, where the quantity of reactive polymer is comprised between 1 and 50% by weight on the mixture.
7. Process according to claim 4 where in the polyamide quantity is comprised between 5 and 20% by weight.
8. Polymeric alloys obtained according to a process of claims 2-7.
9. Manufactured articles obtainable from polymeric alloys of claim 8.

INTERNATIONAL SEARCH REPORT

Inte... onal Application No
PCT/EP 93/02834

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C08L67/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DATABASE WPI Week 8949, Derwent Publications Ltd., London, GB; AN 89-361780 & JP,A,127 660 (UBE INDUSTRIES KK) 31 October 1989 see abstract ---	1-9
Y	EP,A,0 422 282 (PHOBOS N.V.) 17 April 1991 see claims 1-9 ---	1-9
A	DATABASE WPI Week 7141, Derwent Publications Ltd., London, GB; AN 71-66091S & JP,A,46 035 377 (TORAY INDS INC) see abstract ---	1-9
	-/--	

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

1

Date of the actual completion of the international search	Date of mailing of the international search report
11 February 1994	14. 03. 94

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Decocker, L

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 93/02834

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 143 875 (CHEMISCHE WERKE HULS AG) 12 June 1985 see claims 1,2 ---	1-9
A	CHEMICAL ABSTRACTS, vol. 71, no. 22, 1 December 1969, Columbus, Ohio, US; abstract no. 103056t, OKAZAKI, KAORU ET AL 'Modified polyamides' page 81 ; see abstract & JP,A,6 911 669 (TOYO RAYON CO., LTD.) 28 May 1969 ---	1-9
P,A	WO,A,92 17519 (M. & G. RICERCHE S.P.A.) 15 October 1992 see claims 4-7 -----	1-9

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 93/02834

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0422282	17-04-91	AU-B-	631265	19-11-92
		AU-A-	6601090	16-05-91
		DE-A-	4032510	18-04-91
		JP-T-	4505031	03-09-92
		WO-A-	9105815	02-05-91
		US-A-	5243020	07-09-93
EP-A-0143875	12-06-85	DE-A-	3328567	28-02-85
		US-A-	4891406	02-01-90
JP-A-6911669		NONE		
WO-A-9217519	15-10-92	CN-A-	1066856	09-12-92
		EP-A-	0531485	17-03-93